

PATENT SPECIFICATION

NO DRAWINGS

907.926



Date of Application and filing Complete Specification: April 13, 1961.

No. 13330/61.

Application made in United States of America (No. 22701) on April 18, 1960.

Complete Specification Published: Oct. 10, 1962.

Index at acceptance:—Class 2(3), C3A8(A4:B1:C7:J), C3A10D(2:5G1:5G2).

International Classification:—C07c.

COMPLETE SPECIFICATION

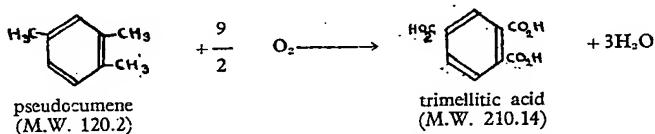
Improvements in or relating to the production of Trimellitic Acid and Trimellitic Anhydride

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

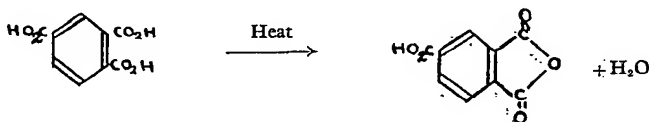
The invention relates to an improved two-

stage process for the preparation of trimellitic acid by oxidation of pseudocumene in the liquid phase. The invention also relates to the subsequent conversion of trimellitic acid to trimellitic anhydride.

It is known to produce trimellitic acid by the oxidation of pseudocumene (1,2,4-trimethyl benzene) according to the reaction:—



Trimellitic acid is converted to trimellitic anhydride by dehydration at temperatures of about 230°C. Thus:



Trimellitic acid

Trimellitic anhydride

Trimellitic acid has been prepared by oxidation of pseudocumene by the various methods used in the oxidation of alkyl-substituted hydrocarbons and related compounds. For example, some text books indicate the oxidation of pseudocumene to trimellitic acid by means of permanganate. On a commercial scale however such a process would be too expensive particularly in view of the fact that the cost of the trimellitic acid must be such that it (and its anhydride) may compete to a certain extent with phthalic acid and phthalic anhydride in price.

According to the present invention a process for the production of trimellitic acid comprises in a first stage oxidising pseudocumene in the liquid phase with a molecular oxygen-containing gas in the presence of a catalyst

comprising a cobalt or manganese salt or mixtures thereof to form a partially oxidised mixture corresponding approximately to the formula $\text{C}_6\text{H}_3(\text{COOH})_x(\text{CH}_3)_{3-x}$, wherein x is within the approximate range 1.3 to 1.8, and in a second stage oxidising said mixture further to trimellitic acid by treatment with nitric acid at an elevated temperature.

The first stage oxidation may be carried out by oxidising pseudocumene with a gas containing molecular oxygen, such as air, in the presence as catalyst of a cobalt salt or a manganese salt or mixture of cobalt and manganese salts, such for example the acetates, nitrates, and naphthenates of these metals. A suitable catalyst mixture comprises, for example, equimolar proportions of manganous nitrate and cobalt nitrate. The proportion

of catalyst used may suitably be from about 0.1 to 4% by weight of the pseudocumene, a preferred amount of catalyst being about 1% by weight. The catalyst is recoverable from the final stages of the process.

The pseudocumene raw material may be pure pseudocumene, or pseudocumene containing aromatic or non-aromatic contaminants. Alternatively the pseudocumene may be diluted with an inert organic liquid diluent. The preferred diluent is a lower aliphatic carboxylic acid, such as acetic acid, although other lower aliphatic acids such as propionic and butyric acids may be used. When used as the diluent acetic acid may be employed in proportions between 1 and 2 parts by weight of acetic acid for each part of pseudocumene.

The first stage oxidation may suitably be carried out at a temperature of about 190°C to about 220°C, and the molecular oxygen-containing gas supplied under moderate pressures, for example, from about 75 p.s.i.g. to about 400 p.s.i.g.

After the first stage oxidation the volatile products of oxidation, any unconverted pseudocumene, and inert diluent, if present, are suitably separated from the desired partial oxidation products of pseudocumene comprising dimethyl benzoic acids and methyl benzene dicarboxylic acids. Such separation may be carried out by vacuum distillation and fractionation leaving the desired partial oxidation products of pseudocumene as residue, or preferably by steam stripping. The inert diluent removed by the separation process may be subsequently condensed and recycled to the first stage oxidation. The partially oxidised residue is passed to the second stage of the process.

The extent of oxidation in the first stage product may be estimated, for instance, by titrating the acid groups formed against standard alkali solution.

In a preferred embodiment, in the second stage the partially oxidised residue stripped of volatile components and inert diluent is diluted with water and brought to about 180°C. Nitric acid of concentration 15—25% is added gradually and continuously. Since each $-\text{CH}_3$ group present in the partially oxidised charge from the first stage consumes nitric acid in order to be converted into a $-\text{COOH}$ group this provides a means for calculating the amount of nitric acid required to complete the oxidation of $\text{C}_6\text{H}_2(\text{COOH})_x(\text{CH}_3)_{3-x}$ to $\text{C}_6\text{H}_4(\text{COOH})_3$.

In the second stage operating temperatures may suitably range from about 170° to about 195°C, temperatures of 180°—185°C being preferred. Operating pressures up to about 220 p.s.i.g. and preferably about 200 p.s.i.g. may be employed.

After addition of the required amount of nitric acid the trimellitic acid is isolated from

the reaction mixture, for example, by crystallisation and the crystals washed and dried.

The catalyst employed is found in the filtrate after removal of the trimellitic acid and may be recovered and recycled to the process.

The nitric acid is itself reduced, chiefly to nitric oxide (NO) although very small amounts may be reduced to N_2O or even to elemental nitrogen. The gases produced in this second stage oxidation, consisting preponderantly of NO and H_2O , are vented from the reaction to a conventional nitric acid recovery system, the recovered nitric acid together with necessary fresh nitric acid as make-up being recycled to the oxidation stage if desired.

The crystal mass of trimellitic acid either before or after drying may be converted to trimellitic anhydride in accordance with a further embodiment of the invention by a heat treatment. Thus the trimellitic acid may be converted to trimellitic anhydride by heating at atmospheric pressure and about 230—235°C, in a dehydration reactor equipped with a heavy agitator. This reactor may be operated continuously, the molten, dehydrated trimellitic anhydride overflowing from the reactor into a crude trimellitic anhydride storage tank through a trap.

The molten trimellitic anhydride may then be purified by distillation in vacuum at 5 mm of mercury or less absolute pressure at 230°—260°C. The temperature during this operation is preferably kept at low as possible within the temperature range indicated, by holding the vacuum at 5 mm or less absolute pressure, since at the higher temperatures, such as 260°C, or above decomposition and coking occur. 90—92% of the theoretically derivable trimellitic anhydride is distilled overhead so that the residue will be fluid. A suitable time of distillation is about 10 hours. The residue to separately distilled under vacuum in a smaller residue distillation still heated as uniformly as possible by a hot liquid jacket (Dowtherm (Registered Trade Mark) for example) with the vacuum held below 5 mm and the heated liquid not about 260°C. If the product from this residue distillation is of inferior colour it may be recycled by adding to a succeeding distillation batch, or enough may be collected from 10—12 runs to permit a full scale distillation. The final residue in the residue distillation still is solid and is removed and discarded. The trimellitic anhydride yield is 93% of theory based on actual trimellitic acid subjected to dehydration.

The process of the invention is further illustrated by the following example, in which parts by weight and parts by volume bear the same relationship to each other as do pounds to gallons (American).

EXAMPLE 1

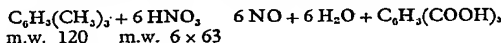
36 parts by weight of 99% assay pseudocumene and 0.42 parts by weight of cobalt nitrate were heated to 200°C in a stainless steel reactor having a back pressure valve which was set at 75 p.s.i.g. Air at 100 p.s.i.g. was passed into the reactor at the rate of 7.95 parts by weight of oxygen per hour and the temperature was maintained at 200—215°C.

The requirement for 36 parts by weight of pseudocumene is 43.1 parts by weight of oxygen for complete conversion to trimellitic acid. At the beginning of the reaction the vented gases contained only 0.2% oxygen, but the rate of air feed was gradually reduced to prevent excessive oxygen escape. Nevertheless, after 3½ hours the exit gases contained about 7% of oxygen at which point the air feed was stopped and the charge allowed to cool to 150°C. At 7% oxygen content the vapours in the condenser were still outside the explosive range. Steam was then passed through the reactor and the charge was steam stripped for 1 hour with 50 parts by weight of steam, and the condensate collected in a recovery condenser cooled by water. The charge during steam

stripping was held at approximately 150°C. The condensate contained about 1.2 parts by weight of an upper layer of hydrocarbon which proved to be pseudocumene and which was separated and oxidised in a subsequent charge. The lower aqueous layer was acid to litmus. Steam was then turned off and the charge cooled to 120°C. A weighed sample of the residual charge was tested for acidity by titration with standard alkali solution and was found to have acid groups equivalent to $C_6H_3(COOH)_{1.5}(CH_3)_{1.7}$.

Then in the same reactor was added 100 parts by weight of water, the back pressure was set at 175 p.s.i.g., and under constant agitation the temperature was raised in the course of 1 hour to 190°C. In this run the vented gases were absorbed in an absorber in which 100 parts by volume of 5% NaOH was circulated by a stainless steel pump. The waste gases from the absorber were conducted to a stack. In large scale operation the vent gases are sent to a nitric acid recovery unit, but on the small scale of the examples such recovery was not necessary.

The theoretical consumption of nitric acid to convert pseudocumene to trimellitic acid is given by the reaction



Thus 120 parts by weight of pseudocumene require 378 parts by weight of 100% nitric acid, or 3.15 parts by weight of 100% HNO_3 , per part by weight of pseudocumene.

The product of the air oxidation, $C_6H_3(COOH)_{1.5}(CH_3)_{1.7}$, would require $1.7/3 \times 3.15$ or 1.785 parts by weight of 100% HNO_3 per part by weight of original pseudocumene. Since the oxidised product represented 34.8 parts by weight of pseudocumene (charge less recovery), it should require 62.118 parts by weight of 100% HNO_3 , or 345.1 parts by weight of 18% HNO_3 by weight. As the result of preliminary runs it was found that approximately 10% excess over theory of nitric acid was actually required to complete the conversion to trimellitic acid; namely in this example, 380 parts by weight of 18% HNO_3 .

380 parts by weight of 18% HNO_3 , namely the theoretical nitric acid plus 10% excess, was pumped into the reactor through an inlet tube leading below the surface of the charge at the rate of 50 parts by weight per hour beginning after the temperature in the charge has reached 190°C. The total time for the addition of all the 18% HNO_3 was 7.6 hours from the start. The temperature was held within the range of 185—195°C, and the pressure at 175 p.s.i.g. After all the nitric acid was added, heating was continued for 1 hour, the charge was then cooled to 90°C and transferred to a stainless steel crystalliser

where it was slowly cooled to 50°C. and allowed to age at this temperature overnight. The crystal mass was centrifuged from the aqueous mixture in a laboratory stainless steel basket centrifuge, washed with a spray of 5 parts by volume of chilled water to remove mother liquor adhering to the crystals, and the crystals were dried to vacuum at 60°C. The yield was 49 parts by volume of crystals. The crystals were faintly yellowish and assayed 99.2% trimellitic acid.

A sample of trimellitic acid of 100 parts by weight, the composite from several runs, was heated to 235°C. with agitation at atmospheric pressure using a condenser with hot water under pressure at 175°C. to remove water and volatiles and to reflux any trimellitic anhydride going over. Heating at 235°C. was continued for 8 hours.

The dehydrated product in the still was distilled the next day under vacuum with absolute pressure not exceeding 5 mm of mercury in the pot and at a temperature between 230°C. and 260°C. The charge containing 99% actual trimellitic acid, and the yield of trimellitic anhydride is theoretically 84.15 parts by weight. When 70 parts by weight of trimellitic anhydride was recovered as distillate in 8 hours, the colour began to darken, and the final portion was collected separately. This final portion weighed 8.3 parts by weight and was light brown to dark brown at the very end. Later redistillation of several com-

bined charges of dark coloured anhydride yielded 96% of good light coloured material. Melting point of the first fraction thus obtained 162°C., assay 98.7%.

EXAMPLE 2

To the stainless steel reactor of Example 1, 12 parts by weight of pure pseudocumene (99%), 20 parts by weight of glacial acetic acid, and 0.21 parts by weight of cobalt acetate and 0.21 parts by weight of manganese nitrate were charged. The back pressure valve was set at 335 p.s.i.g., the temperature was raised to 200°C., and air from a 375 p.s.i.g. source was passed through the reactor at the rate of 2.62 parts by weight of oxygen an hour, and the temperature was held within the range of 205—215°C.

The requirement for 12 parts by weight of pseudocumene is 14.4 parts by weight of oxygen for complete conversion of trimellitic acid. At the beginning of the reaction absorption of oxygen was rapid, but gradually air rate was reduced to maintain a substantially oxygen-free vented gas. After 4 hours the exit gases contained about 7% of oxygen at which point the air feed was stopped and the charge allowed to cool to 110°C. spontaneously and the system pressure released. Steam was then passed through the reactor and the condensate collected. The condensate contained about 0.4 parts by weight of an upper layer of pseudocumene. The steam stripping was continued for 2 hours with heating of the charge to 135°C. and continued agitation. The condensate was assayed and the total acidity was 20.5 parts by weight calculated as acetic acid. Steam was then turned off and the charge cooled to 120°C. The product was found to be equivalent to $C_6H_2(COOH)_{1.4}(CH_3)_{1.4}$ from 11.6 parts by weight of pseudocumene consumed.

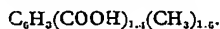
This charge required $1.4/3 \times 3.15$ or 1.47 parts by weight of 100% HNO_3 per part by weight for further oxidation, or 17.05 parts by weight of 100% HNO_3 for the 11.6 parts by weight of pseudocumene consumed. In the form of 18% HNO_3 , this represented 95 parts by weight which with a 10% excess was 104.5 parts by weight of 18% HNO_3 .

To the charge at 120°C. was added 35 parts by weight of water, the temperature was brought, with agitation, in the course of 1 hour to 190°C., and the nitric acid oxidation was run at the same pressure and temperature as in Example 1, but 105 parts by weight of 18% nitric acid was pumped in at the rate of 16 parts by weight per hour, beginning 1 hour after the temperature of the charge had reached 190°C., total time 6½ hours. The crystals were washed with 2 parts by volume of water, total crystal yield after drying 16.15 parts by weight, 79.5% of theory, faintly yellow crystals assaying 98.9% trimellitic acid. The percentage yield of trimellitic anhydride from this material was

practically the same as from the trimellitic acid of Example 1.

EXAMPLE 3

Example 1 was repeated but using a commercial pseudocumene assaying 90% pseudocumene as the hydrocarbon charge, actual pseudocumene 32.4 parts by weight. After the first stage air oxidation and steam stripping the product, a stripped sample showed the empiric composition.



To oxidise this to trimellitic acid with nitric acid would require $31.5 \times 3.15 \times 1.6/3$ or 53.92 parts by weight of 100% HNO_3 theoretically, or 59.3 parts by weight allowing for a 10% excess over theory, or 330 parts by weight of 18% by weight nitric acid.

The second stage oxidation was carried out exactly as in Example 1, and the nitric acid pumped in at the rate of 50 parts by weight per hour required 6½ hours for complete addition. After holding for 1 hour, steaming etc. as in Example 1, the yield was 45 parts by weight of faintly yellowish crystals assaying 99.3% trimellitic acid, about 80% of theory.

WHAT WE CLAIM IS:—

1. A process of the production of trimellitic acid which comprises in a first stage oxidising pseudocumene in the liquid phase with a molecular oxygen-containing gas in the presence as catalyst of a cobalt or manganese salt or mixtures thereof to form a partially oxidised mixture corresponding approximately to the formula



wherein x is within the approximate range 1.3 to 1.8, and in a second stage oxidising said mixture further to trimellitic acid by treatment with nitric acid at an elevated temperature.

2. A process as claimed in claim 1 wherein the free-oxygen-containing gas is air.

3. A process as claimed in claim 2 wherein the free-oxygen-containing gas is supplied as a stream at a pressure of about 75 p.s.i.g. to about 400 p.s.i.g.

4. A process according to any preceding claim wherein the first stage is operated at a temperature of about 190° to about 220°C.

5. A process according to any preceding claim wherein the catalyst comprises cobalt and/or manganese acetate, nitrate, or naphthenate.

6. A process as claimed in claim 5 wherein the catalyst comprises an equimolar mixture of cobalt and manganese nitrate.

7. A process according to any preceding claim wherein the proportion of catalyst employed is from about 0.1 to 4% by weight

of the pseudocumene being oxidised.

8. A process as claimed in claim 7 wherein the proportion of catalyst is about 1% by weight.

9. A process as claimed in Claim 1 wherein the first stage oxidation at least is carried out in the presence of an inert organic liquid diluent.

10. A process as claimed in Claim 9 wherein the diluent is a lower carboxylic acid.

11. A process as claimed in Claim 10 wherein the carboxylic acid is acetic acid.

12. A process as claimed in Claim 9 wherein the diluent and volatile oxidation products are removed before further oxidation of the mixture in the second stage.

13. A process as claimed in Claim 12 wherein the diluent and volatile oxidation products are removed by vacuum distillation and fractionation.

14. A process as claimed in Claim 12 wherein the diluent and volatile oxidation products are removed by steam stripping.

15. A process as claimed in Claim 12 wherein the partially oxidised mixture stripped of diluent and volatile oxidation products is diluted with water and brought to about 180°C before being contacted with nitric acid in the second stage.

16. A process according to any preceding claim employing nitric acid of 15—25% concentration in the second stage.

17. A process according to any preceding claim wherein the oxidation in the second stage is carried out at a temperature of from about 170° to about 195°C.

18. A process as claimed in Claim 17

wherein the oxidation is carried out at 180° to 185°C.

19. A process according to any preceding claim wherein the oxidation in the second stage is carried out at pressures of up to about 220 p.s.i.g.

20. A process according to Claim 19 wherein the oxidation is carried out at about 200 p.s.i.g.

21. A process for the production of trimellitic anhydride which comprises dehydrating trimellitic acid produced by a process according to any of the preceding claims by a heat treatment.

22. A process as claimed in Claim 21 wherein dehydration is effected by heating at atmospheric pressure and at a temperature of about 230° to 235°C.

23. A process as claimed in Claim 21 wherein the trimellitic anhydride is subsequently purified by vacuum distillation at 230° to 260°C.

24. A process for the production of trimellitic acid substantially as hereinbefore described with reference to the Examples.

25. A process for the production of trimellitic anhydride substantially as hereinbefore described with reference to Example 1.

26. Trimellitic acid when produced by a process according to any of claims 1 to 20 and 24.

27. Trimellitic anhydride when produced by a process according to any of claims 21, 22, 23 and 25.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1962. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.